Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Oxidative purification of halogenated ferrocenes

**Michael S. Inkpen, Shuoren Du, Mark Driver, Tim Albrecht,* Nicholas J. Long***

***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***
**DOI: 10.1039/b000000x**

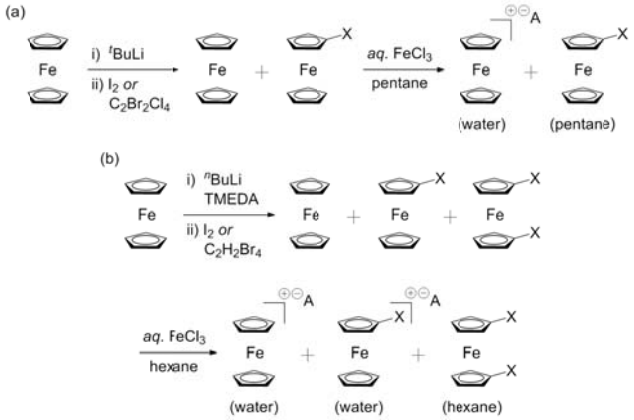
We report the large scale syntheses and 'oxidative purification' of $fcI_2$, $fcBr_2$ and FcBr (fc = ferrocene-1,1'-diyl, Fc = ferrocenyl). These valuable starting materials are typically laborious to separate via conventional techniques, but can be readily isolated by taking advantage of their increased $E_{1/2}$ relative to FcH/FcX contaminants. Our work extends this methodology towards a generic tool for the separation of redox active mixtures.

## Background

Haloferrocenes have a broad reactivity profile, permitting facile preparation of numerous ferrocene-incorporated compounds. For example, direct reactions from Fc–I include Suzuki,[1] Ullmann,[2] Negishi,[3] Stille[4] or Sonogashira[5] couplings, Pd-catalysed carbonylations,[6] aminocarbonylations[7] or phosphinations,[8] and copper mediated processes forming ferrocenyl carboxylic acids[9] or aryl ethers.[10] Indirectly, synthetic possibilities are extended by ready conversion of halogen functionalities to lithium,[11] cyanide,[12] magnesium halide,[13] azide[14] or acetyl[12] species. Ferrocenyl iodides may also be converted to their bromides and chlorides via exchange with CuX (X = Br, Cl) in pyridine.[12]

Despite their versatility, obtaining large quantities of monohaloferrocenes (FcX) or 1,1'-dihaloferrocenes ($fcX_2$) in high purity has never been straightforward. Typical syntheses of the latter (X = Br, I) – via 1,1'-chloromercuriferrocene,[15] 1,1'-dilithioferrocene,[16] 1,l'-bis(tri-n-butylstannyl)ferrocene,[17] 1,1'-ferrocenylenediboronic acid,[18] or other reagents[19] – involve toxic starting materials/intermediates or provide the desired products in difficult to separate mixtures.[17a] Indeed, it has been our experience that reactions of elemental iodine with 1,1'-dilithioferrocene-TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine)[16a] generate a crude product consisting of ferrocene (FcH), FcI and $fcI_2$ (in addition to 1,1'''-diiodobiferrocene and higher order ferrocenes), which is tedious to purify via conventional techniques. In telling examples from the literature, Kovar *et al.* recommend column chromatography of crude $fcI_2$ *using a 2" x 18" column*, or fractional sublimation of crude $fcBr_2$ followed by successive recrystallization.[16a] Others have suggested recrystallization from ethanol/methanol at -30°C.[14,20] Purification problems are likely a result of the monoferrocene series having comparable polarities/solubilities, exacerbated in the case of $fcI_2$, a liquid at room temperature (in contrast to FcI, FcBr and $fcBr_2$, which are solids).

Similar issues with the isolation of FcI were recently discussed by Goeltz and Kubiak,[21] who developed an improved purification procedure based on oxidation potentials (Scheme 1a, X = I).[22] Taking a FcH/FcI mixture in pentane (from lithioferrocene/iodine), they isolated the halogenated product by repeatedly washing the solution with *aq.* $FeCl_3$ (a mild oxidant). This converted the FcH into [FcH]Cl, which was readily extracted into the water layer and removed. By eliminating the need for careful column chromatography/recrystallization, syntheses could be run at large scale – i.e. their published procedure generates 7.03 g FcI from 14.98 g FcH (28% yield).




**Scheme 1** Synthesis and oxidative purification of (a) FcI (Goeltz and Kubiak),[21] and fcBr, and (b) $fcI_2$ and $fcBr_2$ (this work) ($A^- = Cl^-$, $[FeCl_3]^-$ or $[FeCl_4]^-$).

Here we extend this approach, preparing and purifying large quantities of $fcI_2$, $fcBr_2$ and FcBr via oxidation and aqueous extraction of contaminants (Scheme 1). Goeltz and Kubiak's original purification of FcI is revised (in light of new observations), and the compound is produced in improved yield (47% based on FcH) following a readily scalable procedure adapted from Sünkel and Bernhartzeder for FcBr.[23]

## Results and discussion

Mixtures containing FcH, FcX[23-24] and $fcX_2$[16a] (X = Br, I) were prepared as shown in Scheme 1. Based on the previously reported oxidative procedure for purifying FcI,[21] it was considered that an oxidant stronger than $FeCl_3$ ($E°$ Fe(III) + $e^-$ ⇄ Fe(II) = 0.771 V)[25] would be needed to oxidize the FcX components of crude $fcX_2$.

**Table 1** Experimental details for the optimized oxidative purifications of different haloferrocene mixtures.

| compound | FcH (g)[a] | molar ratios of FcH/FcX or FcH/FcX/$fcX_2$[b] | [$FeCl_3$] (M) | # washes *aq.* $FeCl_3$[c] | pure yield (g) | (%) |
|---|---|---|---|---|---|---|
| FcI | 6.0 | 1:17 | 0.2 | 1 | 4.7 | 47 |
| FcBr | 10.0 | 1:11 | 0.2 | 2 | 12.6 | 88 |
| $fcI_2$ | 21.1 | 0.9:1.5:1 | 0.5 | 10 | 9.5 | 19 |
| $fcBr_2$ | 18.6 | 0:1:5.5 | sat. | 2 | 23.0 | 67 |

[a] Indicative of reaction scale. [b] Estimated from $^1$H NMR spectroscopy of the crude product. [c] 1 wash = 200 mL.

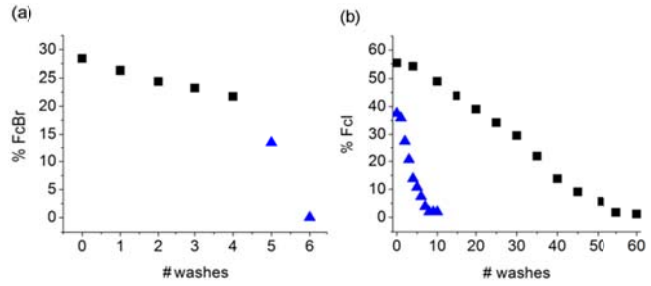



**Fig. 1** (a) The decreasing percentage of FcBr in crude $fcBr_2$ with 4 washings of 200 mL 0.5 M (squares) followed by 2 washings of 200 mL 2.0 M *aq.* $FeCl_3$ (triangles). (b) The decreasing percentage of FcI in crude $fcI_2$ with successive washings of 20 mL (squares) or 200 mL (triangles) 0.5 M *aq.* $FeCl_3$. Compositions estimated by $^1$H NMR, where % FcX + % $fcX_2$ taken as 100%.

Initial work with *n*-hexane solutions of crude $fcI_2$ thus successfully employed AgOTf ($E°$ Ag(I) + $e^-$ ⇄ Ag = 0.7996 V),[25] forming ferrocenium triflates and precipitating silver metal. However, it was soon realized that (the much cheaper) $FeCl_3$ would also oxidize FcX (and given the chance, $fcX_2$). This critical result indicated that FcH/FcX samples were at risk of complete oxidation if the original procedure (using saturated *aq.* $FeCl_3$) was applied too rigorously.

Further investigations showed that selective oxidation could be achieved simply by varying the concentration of *aq.* $FeCl_3$. Procedures are summarized in Table 1, with each washing performed by vigorous shaking or magnetic stirring of the biphasic mixture for *ca.* 2 min. Whilst washes with 0.2 M $FeCl_3$ (200 mL) proved sufficient for removing FcH from mixtures (without significantly affecting FcX), higher concentrations such as 0.5 M or ≥2.0 M could safely be used in purifications of $fcX_2$, more efficiently oxidizing FcI or FcBr, respectively. This is exemplified in Figure 1a, where changing from 0.5 M to 2.0 M $FeCl_3$ greatly reduced the number of washes required to purify a sample of $fcBr_2$. The volume of oxidant solution was also found to play a role, as shown in Figure 1b, where washings with 200 mL 0.5 M $FeCl_3$ were preferable to washings with 20 mL 0.5 M $FeCl_3$ in purifications of crude $fcI_2$.

As expected, the observed order of oxidation, FcH > FcX > $fcX_2$ (and the easier oxidation of iodinated vs. brominated materials), follows the increasing redox potential of these species as measured by cyclic voltammetry ($E_{1/2}$(V) = 0.16 (FcI), 0.17 (FcBr), 0.29 ($fcI_2$) and 0.32 ($fcBr_2$) *vs.* $[FcH]^+/[FcH]$).[†] Each complex exhibits reversible behaviour ($i_{pa}/i_{pc} \approx 1$, $i_p \propto V_s^{1/2}$, $\Delta E \sim$ 0.060 V, as expected for a one-electron process), with measured differences of $E_{1/2}$ (in $CH_3CN$) of 0.16-0.17 V between the oxidation potentials of FcH/FcX and 0.13-0.15 V between those of FcX/$fcX_2$. The difference in these $E_{1/2}$ values indicates that separation of the oxidised species is possible with sufficient selectivity. If the $E_{1/2}$ values are too close then oxidation of one will also lead to oxidation of the other.

## Conclusions

We have developed a methodology towards the large scale synthesis of $fcI_2$, $fcBr_2$, and FcBr. We stress that concentration (and quantity) of oxidizing solutions are crucial to success, and accordingly detail a revised procedure for FcI from previous literature.[21] We suggest that this new purification technique is broadly applicable to redox active mixtures in general (when species are stable in both solution phases, with appropriate $\Delta E_{1/2}$), and should prove a useful addition to the toolkit of methods already available to the practicing synthetic chemist.

## Experimental

### General considerations

All reactions were performed under an atmosphere of nitrogen. Solvents used in reactions were sparged with nitrogen and dried with alumina beads or Q5 copper catalyst on molecular sieves, where appropriate. Silica and neutral alumina of Brockmann activity II (3% $H_2O$) were used for chromatographic separations. Mass spectrometry analyses were conducted by the Mass Spectrometry Service, Imperial College London. $^1$H and $^{13}$C NMR were recorded on a Bruker 400 MHz spectrometer and referenced to the residual solvent peaks of $CDCl_3$ at 7.26 and 77.16 ppm, respectively. Microanalyses were carried out by Stephen Boyer of the Science Centre, London Metropolitan University. FcI was prepared according to literature procedures[16a,21] or via the modified route detailed below, whilst all other reagents were commercially available and used as received.

Cyclic voltammograms were recorded under an atmosphere of argon in MeCN/0.1 M $^n$Bu$_4$NPF$_6$ on a CHI760C potentiostat (CH Instruments, Austin, Texas) with a glassy carbon disc as working electrode (diameter = 2.5 mm), and Pt-wire as reference and counter electrodes respectively. Analyte solutions were between 0.1-1 mM. Potentials are reported relative to an internal $[FcH]^+/[FcH]$ reference.

When washing with solutions of *aq.* $FeCl_3$, extent of oxidation was most accurately monitored by $^1$H NMR spectroscopy. However, removal of contaminants was also indicated by specific experimental observations. Aqueous solutions containing primarily [FcH]A were characterized by a blue-green colour, whereas dark green aqueous solutions containing solid material were typical of [FcI]A. In purifications of $fcI_2$, a lightening of colour and clearing of debris proved indicative of the end point.

In all purifications, it was found necessary to elute materials through a short column (*e.g.* 3″ x 4″, silica/*n*-hexane) to remove oxidized components (as well as higher order ferrocenes and other contaminants, where appropriate). The purity and identify of all products was established by $^1$H/$^{13}$C NMR spectroscopy, accurate mass and elemental analyses.

*n*-Hexane solutions of pure FcH, FcBr and FcI were each oxidised with *aq.* $FeCl_3$ and the resulting aqueous phases

analysed by mass spectrometry. Peaks attributable to $[FcH]^+$, $[FcBr]^+$ and $[FcI]^+$ were observed in positive ion mode, with those attributable to $FeCl_4^-$ and $FeCl_3^-$ seen in negative ion mode.

**1,1'-Diiodoferrocene ($fcI_2$)[16a]**

A mixture of ferrocene (21.14 g, 113.6 mmol), *n*-hexane (100 mL) and TMEDA (37.7 mL, 251.4 mmol) was stirred in an oven-dried 1 L three-necked flask and cooled to 0°C (ice-bath). 2.5 M $^n$BuLi in hexanes (100 mL, 250 mmol) was added via cannula over 5 min, whereby the suspension was slowly raised to ambient temperature and stirred overnight. The resulting bright orange suspension (1,1'-dilithioferrocene-TMEDA) was cooled to -78°C (acetone/dry ice) and a solution of $I_2$ (62.51 g, 246.3 mmol) in diethyl ether (350 mL) added over *ca.* 15 min. After warming to 0°C, the reaction was quenched with water (100 mL) and stirred for a further 15 min. The mixture was extracted with water (3 x 200 mL), dried over $MgSO_4$, and filtered through Celite to provide a dark red oil (*ca.* 33 g) after solvent removal.

The crude product was extracted into *n*-hexane (300 mL) and washed successively with 0.5 M aqueous $FeCl_3$ (*ca.* 10 x 200 mL). When FcH/FcI contaminants had been removed (composition monitored by $^1$H NMR spectroscopy between washings), the organic phase was extracted with water until the washings were colourless, dried over $MgSO_4$, filtered through Celite and evaporated to reveal a brown oil. Further purification via column chromatography (silica/*n*-hexane, 3″ x 4″) and drying *in vacuo* at 50°C yielded pure $fcI_2$ as a dark orange oil (9.54 g, 19%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.18 (pseudo-t, 4H, Cp-*H*, $J$ = 1.68 and 1.78 Hz), 4.37 (pseudo-t, 4H, Cp-*H*, $J$ = 1.88 and 1.81 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 40.42 (Cp–I, *C*I), 72.41 (Cp–I, *C*H), 77.72 (Cp–I, *C*H). HR-MS EI+: *m/z* 437.8065, ($[M]^+$ calc.: 437.8065). (Found: C, 27.58; H, 1.72. Calc. for $C_{10}H_8FeI_2$: C, 27.43; H, 1.84%).

**1,1'-Dibromoferrocene ($fcBr_2$)[16a]**

A mixture of ferrocene (18.60 g, 100 mmol), *n*-hexane (100 mL) and TMEDA (35 mL, 233 mmol) was stirred in an oven-dried 1 L three-necked flask equipped with a pressure-equalizing dropping funnel. After cooling to 0°C (ice-bath), 2.5 M $^n$BuLi in hexanes (85 mL, 212.5 mmol) was added dropwise and the suspension was slowly raised to ambient temperature and stirred overnight. The resulting bright orange precipitate was filtered via cannula, re-suspended in diethyl ether (300 mL), and cooled to -78°C (acetone/dry ice), whereby the funnel was charged with a solution of 1,1,2,2-tetrabromoethane (25 mL, 215 mmol) in diethyl ether (100 mL). This was added to the reaction mixture over a period of 4 h (with vigorous stirring), so as to maintain a temperature of <-70°C. After slowly raising the reaction to ambient temperature and stirring overnight, a two-phase system was produced. The top dark-red layer was decanted (from the bottom black one), quenched with water (50 mL) and separated, providing a dark orange solid after solvent removal.

The crude product was extracted into *n*-hexane (300 mL), filtered through Celite and washed successively with saturated *aq.* $FeCl_3$ (*ca.* 2 × 200 mL). When FcH/FcBr contaminants had been removed (composition monitored by $^1$H NMR spectroscopy between washings), the organic phase was extracted with water until the washings were colourless, dried over $MgSO_4$, and filtered (50 g silica/*n*-hexane). The red solution was dried *in vacuo* to yield pure $fcBr_2$ as an orange solid (23.00 g, 67 %). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.17 (pseudo-t, 4H, Cp-*H*, $J$ = 1.82 and 2.18 Hz), 4.43 (pseudo-t, 4H, Cp-*H*, $J$ = 1.82 and 2.18 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 70.07 (Cp–Br, *C*H), 72.81 (Cp–Br, *C*H), 78.40 (Cp–Br, *C*Br). HR-MS EI+: *m/z* 341.8354, ($[M]^+$ calc.: 341.8342). (Found: C, 35.02; H, 2.38. Calc. for $C_{10}H_8FeBr_2$: C, 34.93; H, 2.35%).

**Bromoferrocene (FcBr)[23]**

A mixture of ferrocene (10.00 g, 53.75 mmol), potassium *tert*-butoxide (0.75 g, 6.68 mmol) and THF (500 mL) was stirred in an oven-dried 1 L three-necked flask. After cooling to -78 °C (acetone/dry ice), 1.9 M $^t$BuLi in pentane (57 mL, 108.3 mmol) was added dropwise. The resulting orange suspension was vigorously stirred for 2 h whereby 1,2-dibromotetrachloroethane (26.25 g, 80.61 mmol) was added against nitrogen. The reaction mixture was stirred for a further 30 minutes at -78°C before slowly warming to ambient temperature, at which point the orange/brown solution was carefully quenched with water, extracted two times with $CH_2Cl_2$ and the solvent removed.

The crude product was extracted into *n*-hexane (300 mL), and washed with 0.2 M *aq.* $FeCl_3$ (*ca.* 2 x 200 mL). When ferrocene had been removed (composition monitored by $^1$H NMR spectroscopy between washings), the organic phase was extracted with water until the washings were colourless, dried over $MgSO_4$ and filtered (50 g silica/*n*-hexane). Evaporation of solvent provided pure FcBr as an orange crystalline solid (12.56 g, 88 %). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.10 (pseudo-t, 2H, Cp-*H*, $J$ = 1.87 Hz), 4.23 (s, 5H, Cp-*H*) 4.41 (pseudo-t, 2H, Cp-*H*, $J$ = 1.84 and 1.87 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 67.21 (Cp–Br, *C*H), 70.24 (Cp–Br, *C*H), 70.73 (Cp, *C*H), 77.76 (Cp–Br, *C*Br). HR-MS EI+: *m/z* 263.9258, ($[M]^+$ calc.: 263.9237). (Found: C, 45.27; H, 3.40. Calc. for $C_{10}H_9FeBr$: C, 45.34; H, 3.42%).

**Iodoferrocene (FcI)**

With an identical procedure to the synthesis of FcBr, the crude solution was produced using ferrocene (6.0 g, 32.3 mmol), potassium *tert*-butoxide (0.45 g, 4.01 mmol), THF (300 mL), 1.9 M $^t$BuLi in pentane (34 mL, 64.6 mmol) and $I_2$ (12 g, 47.3 mmol). This was additionally washed with saturated sodium thiosulfate prior to solvent removal.

The crude product was extracted into *n*-hexane (300 mL), filtered, and washed with 0.2 M *aq.* $FeCl_3$ (1 x 200 mL). When ferrocene had been removed (composition monitored by $^1$H NMR spectroscopy between washings), the organic phase was extracted with water until the washings were colourless, dried over $MgSO_4$, and filtered (30 g silica/*n*-hexane). Evaporation of solvent provided pure FcI as a dark orange solid (4.7 g, 47 %). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.15 (pseudo-t, 2H, Cp-*H*, $J$ = 1.50 and 1.74 Hz), 4.19 (s, 5H, Cp-*H*), 4.41 (pseudo-t, 2H, Cp-*H*, $J$ = 1.75 and 1.51 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 39.85 (Cp–I, *C*I), 68.97 (Cp–I, *C*H), 71.19 (Cp, *C*H), 74.61 (Cp–I, *C*H). HR-MS EI+: *m/z* 311.9104, ($[M]^+$ calcd: 311.9098). (Found: C, 38.12; H, 2.97. Calc. for $C_{10}H_9FeI$: C, 38.50; H, 2.91%).

## Notes and references

*Department of Chemistry, Imperial College London, London SW7 2AZ, U.K.; Tel: +44 (0)20 7594 5781; E-mail: n.long@imperial.ac.uk; t.albrecht@imperial.ac.uk.*

† Electronic Supplementary Information (ESI) available: Electrochemical data and $^{1}H/^{13}C$ NMR spectra for all compounds. See DOI: 10.1039/b000000x/


1. C. Imrie, C. Loubser, P. Engelbrecht and C. W. McCleland, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2513.
2. M. D. Rausch, *J. Org. Chem.*, 1961, **26**, 1802.
3. M. Roemer and D. Lentz, *Chem. Commun.*, 2011, **47**, 7239.
4. M. Roemer and D. Lentz, *Eur. J. Inorg. Chem.*, 2008, **2008**, 4875.
5. A. Kasahara, T. Izumi and M. Maemura, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1021.
6. C. Fehér, Á. Kuik, L. Márk, L. Kollár and R. Skoda-Földes, *J. Organomet. Chem.*, 2009, **694**, 4036.
7. Z. Szarka, R. Skoda-Földes and L. Kollár, *Tetrahedron Lett.*, 2001, **42**, 739.
8. N. F. Blank, J. R. Moncarz, T. J. Brunker, C. Scriban, B. J. Anderson, O. Amir, D. S. Glueck, L. N. Zakharov, J. A. Golen, C. D. Incarvito and A. L. Rheingold, *J. Am. Chem. Soc.*, 2007, **129**, 6847.
9. M. Sato, H. Nakahara, K. Fukuda and S. Akabori, *J. Chem. Soc., Chem. Commun.*, 1988, 24.
10. M. R. an der Heiden, G. D. Frey and H. Plenio, *Organometallics*, 2004, **23**, 3548.
11. A. R. Koray, M. Ertas and Ö. Bekaroglu, *J. Organomet. Chem.*, 1987, **319**, 99.
12. M. Sato, T. Ito, I. Motoyama, K. Watanabe and K. Hata, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1976.
13. (a) H. Shechter and J. F. Helling, *J. Org. Chem.*, 1961, **26**, 1034; (b) K. Sanechika, T. Yamamoto and A. Yamamoto, *Polym. J.*, 1981, **13**, 255.
14. A. Shafir, M. P. Power, G. D. Whitener and J. Arnold, *Organometallics*, 2000, **19**, 3978.
15. (a) A. N. Nesmeyanov, E. G. Perevalova and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, 1955, **100**, 1099; (b) A. N. Nesmeyanov, V. A. Sazonova and V. I. Romanenko, *Dokl. Akad. Nauk SSSR*, 1965, **161**, 1085; (c) R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 1965, **30**, 1253; (d) R. W. Wagner, T. E. Johnson and J. S. Lindsey, *Tetrahedron*, 1997, **53**, 6755; (e) V. A. Nefedov and M. N. Nefedova, *Zh. Obshch. Khim.*, 1966, **36**, 122.
16. (a) R. F. Kovar, M. D. Rausch and H. Rosenberg, *Organomet. Chem. Synth.*, 1971, **1**, 173; (b) M. Kai, I. Motoyama, M. Katada, Y. Masuda and H. Sano, *Chem. Lett.*, 1988, 1037; (c) Q. Lu, X.-H. Wang and F.-S. Wang, *Chin. J. Appl. Chem.*, 2011, **28**, 136; (d) M. A. Bakar, N. N. Sergeeva, T. Juillard and M. O. Senge, *Organometallics*, 2011, **30**, 3225; (e) T.-Y. Dong and L.-L. Lai, *J. Organomet. Chem.*, 1996, **509**, 131.
17. (a) I. R. Butler, S. B. Wilkes, S. J. Mcdonald, L. J. Hobson, A. Taralp and C. P. Wilde, *Polyhedron*, 1993, **12**, 129; (b) P. Park, A. J. Lough and D. A. Foucher, *Macromolecules*, 2002, **35**, 3810; (c) C.-H. Andersson, L. Nyholm and H. Grennberg, *Dalton Trans.*, 2012, **41**, 2374.
18. (a) A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd, *Dokl. Akad. Nauk SSSR*, 1959, **126**, 1004; (b) A. N. Nesmeyanov, V. A. Sazonova and V. N. Drosd, *Chem. Ber.*, 1960, **93**, 2717.
19. (a) W. A. Herrmann and M. Huber, *Chem. Ber.*, 1978, **111**, 3124; (b) B. G. Conway and M. D. Rausch, *Organometallics*, 1985, **4**, 688.
20. S. Sorriso, G. Cardaci and S. M. Murgia, *J. Organomet. Chem.*, 1972, **44**, 181.
21. J. C. Goeltz and C. P. Kubiak, *Organometallics*, 2011, **30**, 3908.
22. We note that another purification method based on redox potentials has been reported earlier, but this has not yet been widely embraced. See: K. L. Cunningham and D. R. McMillin, *Polyhedron*, 1996, **15**, 1673.
23. K. Sünkel and S. Bernhartzeder, *J. Organomet. Chem.*, 2011, **696**, 1536.
24. (a) D. Guillaneux and H. B. Kagan, *J. Org. Chem.*, 1995, **60**, 2502; (b) R. Sanders and U. T. Mueller-Westerhoff, *J. Organomet. Chem.*, 1996, **512**, 219.
25. *CRC Handbook of Chemistry and Physics* (92nd ed.), ed. W. M. Haynes, CRC Press, 2011-2012.